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Stability studies of the electrical conductivity of poly(pyrrole tosylate) (PPTOS); poly(pyrrole dodecylbenzenesulfonate) (PPDBS) and polypyrrole/poly(styrene sulfonate) (PP/PSS) films and their laminated / composites with epoxy/glass have been carried out at 160°F and 95% relative humidity. GPC molecular weight studies of poly(3-alkylthiophenes) has shown that the use of a multiangle laser light scattering (MALLS) detector, which provides absolute molecular weights, gives much higher values (2-5 times) than using polystyrene standards and an RI or UV-VIS detector. Thus, polystyrene is a poor molecular weight standard for these rigid rod poly(3-alkylthiophenes). Ion binding studies have been extended to polypyrrole/poly(styrene sulfonate) using $Ru(bpy)_3^{(2+)}$ (bpy = 2,2'-bipyridyl) and $Ru(NH_3)_6^{(3+)}$ as redox probes. Copolymers of pyrrole and 3-(1-pyrrolyl)propanesulfonate have also been studied this way. Partition coefficients were determined with a combination of UV-VIS spectrophotometric and voltammetric data.

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Electronic and Ionic Transport in Processable Conducting Polymers

by

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January 10, 1990

Description of Progress

Stability studies of the electrical conductivity of poly(pyrrole tosylate) (PPTOS), poly(pyrrole dodecylbenzenesulfonate) (PPDBS) and polypyrrole/poly(styrene sulfonate) films (PP/PPS) and their laminated composites with epoxy/glass has continued. In a comparitive study treating the polymers at 160 °F and 95% relative humidity, PPTOS and PPDBS films prepared in our laboratory exhibited a higher conductivity and greater stability than either polypyrrole film prepared by BASF (Germany) or polypyrrole on quartz prepared by Milliken Research Corporation. Epoxy laminated films exhibited higher stability at 160 °F and 95% relative humidity when compared to free standing films.

We have examined samples of poly(3-alkylthiophene), prepared by our $FeCl_3$ and oxygen/air polymerization process, by gel permeation chromatography using polystyrene standards. We have noted that the number average (M_N) and weight average (M_W) molecular weights using a refractive index detector are somewhat different from those obtained using a UV-VIS detector. More importantly, the M_N and M_W values obtained using our newly acquired multiangle laser light scattering (MALLS) detector, which gives absolute molecular weights, are very much larger (2-5 times) than those obtained using the other detectors. Thus it is clear that polystyrene is a rather poor standard for the rigid rod poly(3-alkylthiophene) polymers.

Blends of poly(decylthiophene) with low density polyethylene have been prepared and have been spun into fibers by Hoechst-Celanese. Preliminary evidence is that the blending improves the spinning performance relative to pure poly(3-decylthiophene).

The ion binding studies have been extended to polypyrrole/poly(styrene sulfonate) using $Ru(bpy)_3^{2+}$ and (bpy = 2,2'-bipyridyl) and $Ru(NH_3)_6^{3+}$ as redox probes. Partition coefficients were derived using a combination of UV/VIS spectrophotometric and voltammetric data. Corresponding studies on copolymers of pyrrole and 3-(1-pyrrolyl)propanesulfonate have been completed. New studies have been initiated on the binding of $Fe(CN)_6^{3-/4-}$ by poly(vinylpyridine) films and in situ photochemical conversion of these immobilized moieties to Prussian Blue catalyst.

Mechanistic studies of this conversion process in homogeneous situations are also in progress using UV/VIS spectrophotometry and voltammetry. The use of fluorophore-containing polypyrrole films [e.g. poly(pyrrole naphthalenesulfonate)] for partitioning of the capacitive and faradaic charge during redox switching is also under study.

Publications

Papers Published

Reynolds, J. R., Hsu, S. G. and Arnott, H. J., "The Effect of Growth Morphology on the Electrochemical Response of Poly(3-methylthiophene)," *J. Polym. Sci., Polym. Phys. Ed.*, **1989**, *27*, 2081-2103.

Tsai, E. W., Basak, S., Ruiz, J. P., Reynolds, J. R. and Rajeshwar, K., "Electrochemistry of Some β-Substituted Polythiophenes. Anodic Oxidation, Electrochromism and Electrochemical Deactivation Behavior," *J. Electrochem. Soc.*, **1989**, *136*, 3683-3689.

Basak, S., Nayak, K., Marynick, D. S. and Rajeshwar, K., "Synthesis, Characterization, Theoretical Modeling and Polymerization of New Fluorophore-Containing Derivatives of Thiophene and Pyrrole," *Chemistry of Materials*, **1989**, *1*, 611-619.

Shaffer, T. D., "Phase Transfer Catalyzed Polyetherification Through Nitro Displacement," *J. Polym. Sci., Polym. Lett. Ed.*, **1989**, *27*, 457-464.

Ho, Y.-H., Basak, S., Tsai, E. W. and Rajeshwar, K., "Optical Probes of Ion Transport in Electrochemical Processes Based on In Situ Derivatization: Monitoring of Ion Transport and Assay of Doping Levels in Polypyrole and Polythiophene Membranes," *J. Chem. Soc., Chem. Commun.*, **1989**, 1078-1080.

Papers in Press

Shaffer, T. D. and Kramer, M. C., "Cyclization vs. Polymerization in Phase Transfer Catalyzed Polythioetherification," *Makromol. Chem.*, in press.

Nayak, K. and Marynick, D. S., "The Interplay Between the Geometric and Electronic Structures of Polyisothianaphthene and Polyisonaphthothiophene, Polythieno(3,4-b)pyrazine and Polythieno(3,4-b)quinoxaline," *Macromolecules*, in press.

Qiu, Y.-J. and Reynolds, J. R., "Poly[3,6-(carbaz-9-yl)propanesulfonate]: A Self-Doped Polymer with Both Cation and Anion Exchange Properties," *J. Electrochem. Soc.*, in press.

Sharma, S. C., Krishnamoorthy, S., Naidu, S. V., Eom, C. I., Krichene, S. and Reynolds, J. R., "Positron Annihilation and Conductivity Measurements on Poly(pyrrole tosylate) and Poly(pyrrole fluoride)," *Phys. Rev. B.*, in press.

Papers Submitted for Publication

Reynolds, J. R. and Pomerantz, M., "Processable Electronically Conducting Polymers" in "Electroresponsive Molecular and Polymeric Systems"; Skotheim, T. A., Ed.; Marcel Dekker: New York; Vol. 2; submitted for publication.

Gieselman, M. G. and Reynolds, J. R., "Poly(*p*-phenyleneterephthalamide propanesulfonate): A New Polyelectrolyte for Application to Conducting Molecular Composites," *Macromolecules*, submitted for publication.

Baker, C. K., Qiu, Y. J. and Reynolds, J. R., "Electrochemically Induced Mass Transport in Poly(pyrrole)/Poly(styrene sulfonate) Molecular Composites," *J. Am. Chem. Soc.*, submitted for publication.

Basak, S., Rajeshwar, K. and Kaneko, M., "Ion Binding of Poly{Pyrrole-Co[3-(Pyrrol-1-yl)Propane Sulfonate]} Thin Films," *Anal. Chem.*, submitted for publication.

Wang, F. and Reynolds, J. R., "Soluble and Electroactive Nickel Bis(dithiolene) Polymers Prepared Via Metal Complexation Polymerization," *Macromolecules*, submitted for publication.

Shaffer, T. D. and Sheth, K. A., "Mesomorphic Polyazomethine Ethers Containing Dibenzo-18-crown-6 Units," *Makromol. Chem., Rapid Commun.*, submitted for publication.

New Major Equipment

A Spex Ramalog Raman spectrometer is being installed. This system will be used for the study of ion transport during redox switching of conducting polymers.

Meetings Attended and Talks Presented

Martin Pomerantz and Dennis S. Marynick attended The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 17-22, 1989. The following paper was presented in the Macromolecular Chemistry section:

> Tseng, J. J.; Uitz, R.; Pomerantz, M.; Reynolds, J. R.; Arnott, H. J. and Haider, I., "Poly(3-alkylthiophenes). Synthesis Melt and Solution Processability".

John R. Reynolds attended the Materials Research Society, 1989 Fall Meeting, Boston, MA, November, 1989 and presented the following paper:

> Ruiz, J. P.; Nayak, K.; Reynolds, J. R. and Marynick, D. S., "Heterocyclic Polymers and Copolymers With Controlled Optoelectronic Properties".

John Reynolds visited Enichem Inc. in Monmouth Junction, NJ in November, presented a seminar entitled "Electronic and Ionic Transport in Conducting Polyheterocycles" and discussed possibilities of collaborative research.

Krishnan Rajeshwar gave an invited seminar entitled "Ion Transport in Conductive Polymers" at the Chemistry Department, Drexel University in September, 1989. Discussions were also held with Professors A. MacDiarmid of The University of Pennsylvania and Yen Wei during this visit.

Visitors to UTA

Professor Michael Hanack of The University of Tübingen, West Germany visited our laboratories on December 5, 1989 and presented a seminar entitled "Bridged Macrocyclic Metal Complexes. A New Concept for Semiconducting Materials".

Professor Adam Heller of The University of Texas at Austin visited UTA on December 8, 1989 and presented a seminar entitled "Electrical Wiring of Redox Enzymes".

Professor John P. Ferraris of The University of Texas at Dallas visited our laboratories on November 3, 1989 and presented a seminar entitled "Steric Effects on the Optical and Electrochemical Properties of Polyheteroaromatics".